



COPY OF PAPERS
ORIGINALLY FILED

RECEIVED
AUG 22 2002
TECHNOLOGY CENTER 2800

(19) Japan Patent Office (JP)
(12) KOKAI TOKKYO KOHO (A)
(11) Laid-open Application Number: 2001-189296 (P2001-189296A)
(43) Publication Date: July 10, 2001

(51) Int. Cl. ⁷	Id. Symbol	F1	Theme code (reference)
H 01 L 21/304	622	H 01 L 21/304	622X 3C058
B 24 B 37/00		B 24 B 37/00	H 5F033
C 09 K 3/00		C 09 K 3/00	
H 01 L 21/3205		H 01 L 21/88	

Examination Request: Filed

No. of Claims: 19 (total pages 18)

(21) Application No.: Heisei 11-374487
(22) Application Filed: December 12, 1999

(71) Applicant: NEC CORP.
Address: 7-1, Ibaraki 5-chome, Minato-ku, Tokyo, Japan
(72) Inventor: Yasuaki Tsuchiya
Address: 7-1, Ibaraki 5 chome, Minato-ku, Tokyo, Japan
c/o NEC CORP.
(72) Inventor: Tomoko Wake.
Address: 7-1, Ibaraki 5 chome, Minato-ku, Tokyo, Japan
c/o NEC CORP.
(74) Patent Representative: 100088328
Patent Attorney: S. Kaneda (and two more representatives)

Continued on the last page.

Specification

(54) [Title of the Invention] METHOD FOR FORMING METAL WIRING

(Abstract)

[Object] The object of the present invention is to provide a method for forming a metal wiring, which makes it possible to suppress the occurrence of ditching and erosion and to form a highly reliable embedded wiring with a small spread of wiring resistance.

[Means to Attain the Object] A method for forming a metal wiring, comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on the electrically insulating film, forming a metal film for wiring over the entire surface so as to fill the recess, and polishing the substrate surface by a chemical-mechanical polishing method, wherein the polishing step comprises a first polishing step in which polishing is conducted so that the metal film for wiring partially remains on the surface outside the recess and

a second polishing step in which polishing is conducted till the surface of the electrically insulating film outside the recess is almost entirely exposed, by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no less than 1 and no more than 3.

[Patent Claims]

[Claim 1] A method for forming a metal wiring comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on said electrically insulating film, forming a metal film for wiring over the entire surface so as to fill said recess, and polishing the substrate surface by a chemical-mechanical polishing method, wherein said polishing step comprises a first polishing step in which polishing is conducted so that the metal film for wiring partially remains on the surface outside said recess and a second polishing step in which polishing is conducted till the surface of the electrically insulating film outside said recess is almost entirely exposed, by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no less than 1 and no more than 3.

[Claim 2] The method for forming a metal wiring, as described in Claim 1, wherein in the first polishing step, polishing is conducted so that the metal film for wiring remains at a surface area ratio of no less than 5% and no more than 30% of the substrate surface outside the recess.

[Claim 3] The method for forming a metal wiring, as described in Claim 1 or Claim 2, wherein in the first polishing process, polishing is conducted by using a polishing slurry comprising a polishing material, an oxidizing agent, an organic acid, and an alkanolamine represented by the following general formula (1).



(in this formula, R^1 stands for a hydrogen atom or an alkyl group containing no less than 1 and no more than 5 carbon atoms, R^2 stands for an alkyl group containing no less than 1 and no more than 5 carbon atoms, m is integer of no less than 0 and no more than 2, n is a natural number of no less than 1 and no more than 3, $m + n = 3$).

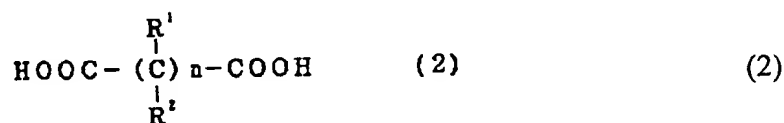
[Claim 4] A method for forming a metal wiring, comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on said electrically insulating film, forming a metal film for wiring over the entire surface so as to fill said recess, and polishing the substrate surface by a chemical-mechanical polishing method, wherein said polishing step comprises a first polishing step in which polishing is conducted by using a polishing slurry comprising a polishing material, an oxidizing agent, an organic acid, and an alkanolamine represented by the above-described general formula (1), so that the metal film for wiring does not remain on the surface outside said recess and so that the barrier metal film is not completely removed by polishing, and a second polishing step in which polishing is conducted till the surface of the electrically insulating film outside said recess is almost entirely exposed, by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no more than 1.

[Claim 5] The method for forming a metal wiring, as described in Claim 3 or Claim 4, wherein a polishing slurry is used which contains no less than one compound selected from the group including ethanolamine, diethanolamine, and triethanolamine as said alkanolamine.

[Claim 6] The method for forming a metal wiring, as described in Claim 1, wherein in the second polishing step, a polishing slurry is used which provides for a polishing rate ratio of the electrically insulating film to the barrier metal of no less than 0.01 and no more than 0.5.

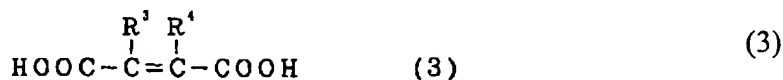
[Claim 7] The method for forming a metal wiring, as described in any claim from Claim 1 to Claim 6, wherein in the second polishing step, a polishing slurry is used which comprises a silica polishing material and a carboxylic acid represented by the following general formula (2) or (3).

[Chemical Formula 1]



(n is any one from 0, 1, 2, 3; R¹ and R² represent hydrogen atoms, -OH, or -COOH independently for each carbon atom to which they are bonded).

[Chemical Formula 2]



(R³ and R⁴ represent hydrogen atoms or -OH, independently from each other).

[Claim 8] The method for forming a metal wiring, as described in Claim 7, wherein a polishing slurry is used which contains at least one acid selected from the group including oxalic acid, malonic acid, tartaric acid, malic acid, glutaric acid, citric acid, and maleic acid as said carboxylic acid.

[Claim 9] The method for forming a metal wiring, as described in any claim from Claim 1 to Claim 8, wherein in said second polishing step, wiring is conducted by using a polishing slurry comprising a silica polishing material and an inorganic salt.

[Claim 10] The method for forming a metal wiring, as described in Claim 9, wherein polishing is conducted by using a polishing slurry comprising at least one compound selected from the group including salts of hydrogenacids, salts of oxo acids, salts of peroxo acids, and halogen oxo acid salts.

[Claim 11] A method for forming a metal wiring comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on said electrically insulating film, forming a metal film for wiring over the entire surface so as to fill said recess,

and polishing the substrate surface by a chemical-mechanical polishing method using a polishing slurry comprising a silica polishing material and a carboxylic acid represented by the general formula (2) or (3).

[Claim 12] The method for forming a metal wiring, as described in Claim 11, wherein polishing is conducted by using a polishing slurry which contains at least one acid selected from the group including oxalic acid, malonic acid, tartaric acid, malic acid, glutaric acid, citric acid, and maleic acid as said carboxylic acid.

[Claim 13] A method for forming a metal wiring comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on said electrically insulating film, forming a metal film for wiring over the entire surface so as to fill said recess, and polishing the substrate surface by a chemical-mechanical polishing method using a polishing slurry comprising a silica polishing material and an inorganic salt.

[Claim 14] The method for forming a metal wiring, as described in Claim 13, wherein polishing is conducted by using a polishing slurry comprising at least one compound selected from the group including salts of hydrogenacids, salts of oxo acids, salts of peroxo acids, and halogen oxo acid salts.

[Claim 15] The method for forming a metal wiring, as described in any claim from Claim 7 to Claim 14, wherein said polishing slurry comprises an oxidizing agent.

[Claim 16] The method for forming a metal wiring, as described in Claim 15, wherein said polishing slurry comprises an oxidation-preventing agent.

[Claim 17] The method for forming a metal wiring, as described in Claim 16, wherein said polishing slurry comprises benzotriazole or derivative thereof as the oxidation-preventing agent.

[Claim 18] The method for forming a metal wiring, as described in any claim from Claim 1 to Claim 17, wherein said barrier metal film is a tantalum-type metal film.

[Claim 19] The method for forming a metal wiring, as described in any claim from Claim 1 to Claim 18, wherein said barrier metal film is a copper or copper alloy film.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Utilization] The present invention relates to a method for forming an embedded metal wiring by using chemical-mechanical polishing, this method being suitable for the manufacture of semiconductor devices.

[0002]

[Prior Art Technology] The conventional method for forming an embedded wiring comprises the steps of forming a recess such as a groove or a contact hole in an electrically insulating film formed on a substrate, forming a barrier metal film on the electrically insulating film, forming an electrically conductive metal film over the entire surface so as to fill the recess, and then conducting polishing of the surface by chemical-mechanical polishing (referred to as CMP hereinbelow). The formation of a copper embedded wiring will be described below as an example of such conventional method.

[0003] Because of its excellent resistant to electromigration and low resistance, copper has attracted attention as an extremely useful electric contact material in the fabrication of semiconductor integrated circuits such as ULSI whose miniaturization and integration have been going at an accelerated pace in recent years.

[0004] Because problems such are associated with the formation of wiring by using copper (for example, patterning is difficult to conduct by dry etching), an embedded wiring formation method which employed the above-mentioned CMP is presently used. Thus, a recess such as a groove or a contact hole is formed in an insulating film, a barrier metal film is formed, then a copper film is deposited over the entire surface by plating so as to fill the recess, and then the surface is planarized by conducting polishing by the CMP method till the entire surface of the electrically insulating film outside the recess is exposed. As a result, an embedded copper wiring or electric contact such as a via plug, contact plug, and the like, is formed in which copper is embedded in the recess.

[0005] A method for forming an embedded copper wiring will be described below with reference to FIG. 1.

[0006] First, as shown in FIG. 1(a), a silicon nitride film 2 and a silicon oxide film 3 are formed in the order of description on a silicon substrate 1. Then, a recess reaching the silicon nitride film 2 and having a wiring pattern shape is formed in the silicon oxide film 3.

[0007] Then, as shown in FIG. 1(b), a barrier metal film 4 is formed by a sputtering method. A copper film 5 is formed thereupon by a plating method so as to fill the recess.

[0008] The copper film 5 is then polished and the substrate surface is planarized by CMP, as shown in FIG. 1(c). Polishing by CMP is continued till the entire metal present on the silicon oxide film 3 is removed.

[0009]

[Problems Addressed by the Present Invention] In the above-described formation of the embedded metal wiring, a barrier metal film is formed as an underlying film to prevent diffusion of wiring metal into the electrically insulating film. However, if a metal with a very high chemical stability, such as a tantalum-type metal (for example, Ta or TaN), is used when CMP using the conventional polishing slurry is conducted, the polishing rate of the barrier metal film is lower than that of the wiring metal film, that is, there is a difference in the polishing rate

between the wiring metal film and the barrier metal film, and this difference causes erosion or ditching.

[0010] Ditching is a state in which, as shown in FIG. 2, the wiring metal present inside a recess is overpolished and the central portion of the wiring metal film located inside the recess has receded with respect to the flat surface of the electrically insulating film on the substrate. In CMP using conventional polishing slurries, the polishing rate of barrier metal film is low. As a result, a sufficient polishing time has to be selected in order to remove the entire barrier metal film 4 present on the electrically insulating film (silicon oxide film 3). However, since the polishing rate of wiring metal film (copper film 5) is higher than that of the barrier metal film 4, the wiring metal film (copper film 5) is overpolished, which results in ditching.

[0011] On the other hand, erosion, as shown in FIG. 1(d), is a state in which polishing of the region with a high wiring density proceeds in excess when compared with that of the regions with a low wiring density, which results in recession of the regions with a high wiring density with respect to other regions. If polishing of wiring metal film (copper film 5) proceeds faster than that of the barrier metal film 4 or electrically insulating film (silicon oxide film 3) when regions with a high wiring density, in which a large number of the embedded portions of wiring metal film (copper film 5) are present, and regions with an isolated wiring, in which the embedded portions of wiring metal film (copper film 5) are practically not present, are significantly separated from each other inside a wafer by a wiring-free regions or the like, then in the regions with a high wiring density the polishing pad pressure applied to the barrier metal film 4 or electrically insulating film (silicon oxide film 3) will be higher than that in the regions with isolated wiring. As a result, in the CMP process conducted after the barrier metal film 4 has been exposed (process after step 1(c)), the polishing rate becomes different in the regions with a high density of wiring and regions with an isolated wiring, and the electrically insulating film in the regions with a high wiring density is polished in excess, thereby causing erosion.

[0012] As described above, if ditching occurs in the process for forming an embedded wiring of semiconductor devices, the wiring resistance or connection resistance is increased and electromigration can easily occur. As a consequence, the reliability of elements is degraded. Further, if erosion occurs, planarization of the substrate surface is degraded, this defect being even more evident in multilayer structures. Therefore, problems such as increase or spread in the wiring resistance cannot be avoided.

[0013] Japanese Laid-open Patent Application No. 8-83780 disclosed a method for preventing the above-mentioned ditching in the CMP process by introducing benzotriazole or a derivative thereof into a polishing slurry and forming a protective film on the surface of Cu. Further, Japanese Laid-open Patent Application No. 11-238709 also described a ditching-preventing effect of triazole compounds. However, with the above-mentioned method, ditching is suppressed by decreasing the polishing rate of copper film and though the difference in the polishing rate between the copper film and the barrier metal film is decreased, the polishing time of copper film is extended and throughput is decreased. Moreover, a problem associated with erosion is not discussed in the specifications of those applications.

[0014] Further, Japanese Laid-open Patent Application No. 10-44047, in the section thereof relating to embodiments, disclosed that if CMP is conducted by using a polishing slurry comprising an alumina polishing material, ammonium persulfate (oxidizing agent) and a specific carboxylic acid, the difference in the polishing rate between the aluminum layer for wiring and silicon oxide is increased and the removal rate of titanium film employed for a barrier metal film is also increased. However, the method disclosed in the embodiments failed to resolve the above-described problems of ditching and erosion when a metal with an extremely high chemical stability, such as a tantalum-type metal, was used for the barrier metal film.

[0015] Japanese Laid-open Patent Application No. 10-46140 disclosed a composition for chemical-mechanical polishing which comprised a specific carboxylic acid, an oxidizing agent, and water and had a pH value adjusted to 5-9 with an alkali. In the embodiments, polishing compositions containing malic acid, citric acid, tartaric acid, or oxalic acid as the carboxylic acid and aluminum oxide as the polishing material (Embodiments 1-4, 7, 8, 11) and a polishing composition containing malic acid as the carboxylic acid and silicon oxide as the polishing material (Embodiment 12) were disclosed. However, in the specification, the effect of carboxylic acid (e.g., citric acid) addition was described with respect to the prevention of ditching which is caused by increase in polishing rate and formation of corrosion dimples, and polishing of the barrier metal film and erosion were not mentioned.

[0016] Further, Japanese Laid-open Patent Application No. 10-163141 disclosed a composition for polishing a copper film, which comprises a polishing material and water, the specific feature of this composition being that it additionally contains an iron (III) compound present in the composition in a dissolved state. In the embodiments, colloidal silica was used as the polishing agent and iron (III) citrate, ammonium iron (III) citrate, and ammonium iron (III) oxalate were used as the iron (III) compound. Such compositions were shown to increase the polishing rate of copper film and to suppress the appearance of defects such as ditching or scratches. However, this specification, too, failed to mention erosion or polishing of the barrier metal film consisting of metals with an extremely high chemical stability, such as a tantalum-type metal.

[0017] Further, Japanese Laid-open Patent Application No. 11-21546 disclosed a slurry for chemical-mechanical polishing comprising urea, a polishing material, an oxidizing agent, a film-forming agent, and a complex-forming agent. Examples of polishing Cu, Ta, and PTEOS were disclosed in which polishing was conducted with a slurry with pH 7.5 was prepared by using alumina as the polishing material, hydrogen peroxide as the oxidizing agent, benzotriazole as the film-forming agent, and tartaric acid or ammonium oxalate as a complex-forming agent. However, in the specification, disturbance of a passivation layer formed by the film-forming agent such as benzotriazole and the limitation placed on the oxidation layer depth were the only reported effects of the addition of the complex-forming agent such as tartaric acid or ammonium oxalate. Though Ta and TaN were presented as examples of barrier metals, no reference was made to erosion or polishing effect with respect to the barrier metal film composed of a metal with extremely high chemical stability, such as tantalum-type metal.

[0018] With the foregoing in view, it is an object of the present invention to provide a method for forming a metal wiring, which makes it possible to suppress the occurrence of ditching or erosion and to form a highly reliable embedded wiring with a small spread of wiring resistance.

[0019]

[Means to Attain the Object] The present invention provides a method for forming a metal wiring comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on the electrically insulating film, forming a metal film for wiring over the entire surface so as to fill the recess, and polishing the substrate surface by a chemical-mechanical polishing method, wherein the polishing step comprises a first polishing step in which polishing is conducted so that the metal film for wiring partially remains on the surface outside the recess and a second polishing step in which polishing is conducted till the surface of the electrically insulating film outside the recess is almost entirely exposed, by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no less than 1 and no more than 3.

[0020] The present invention also relates to the above-described method for forming a metal wiring in accordance with the present invention, wherein in the first polishing process, polishing is conducted by using a polishing slurry comprising a polishing material, an oxidizing agent, an organic acid, and an alkanolamine represented by the following general formula (1).

[0021]



(in this formula, R^1 stands for a hydrogen atom or an alkyl group containing no less than 1 and no more than 5 carbon atoms, R^2 stands for an alkyl group containing no less than 1 and no more than 5 carbon atoms, m is integer of no less than 0 and no more than 2, n is a natural number of no less than 1 and no more than 3, $m + n = 3$).

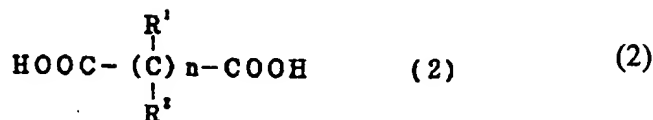
[0022] Further, the present invention also relates to a method for forming a metal wiring comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on the electrically insulating film, forming a metal film for wiring over the entire surface so as to fill the recess, and polishing the substrate surface by a chemical-mechanical polishing method, wherein the polishing step comprises a first polishing step in which polishing is conducted by using a polishing slurry comprising a polishing material, an oxidizing agent, an organic acid, and an alkanolamine represented by the above-described general formula (1), so that the metal film for wiring does not remain on the surface outside the recess and so that the barrier metal film is not completely removed by polishing, and a second polishing step in which polishing is conducted till the surface of the electrically insulating film outside the recess is almost entirely exposed, by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no more than 1.

[0023] The present invention also relates to a method for forming a metal wiring comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on the electrically insulating film, forming a metal film for wiring over the entire surface so as to fill the recess, and polishing the substrate surface by a chemical-

mechanical polishing method using a polishing slurry comprising a silica polishing material and a carboxylic acid represented by the general formula (2) or (3).

[0024]

[Chemical Formula 3]



(n is any one from 0, 1, 2, 3; R¹ and R² represent a hydrogen atom, -OH, or -COOH independently for each carbon atom to which they are bonded).

[0025]

[Chemical Formula 4]



(R³ and R⁴ represent hydrogen atoms or -OH, independently from each other).

[0026] The present invention also relates to a method for forming a metal wiring comprising the steps of forming a recess in an electrically insulating film formed on a substrate, forming a barrier metal film on the electrically insulating film, forming a metal film for wiring over the entire surface so as to fill the recess, and polishing the substrate surface by a chemical-mechanical polishing method using a polishing slurry comprising a silica polishing material and an inorganic salt.

[0027] Further, in accordance with the present invention, the term "recess" stands for a groove or a connection hole such as a contact hole or through hole for the formation of embedded wiring. Further, the expression "the insulating film formed on the substrate" includes the interlayer insulating film formed on the lower wiring layer.

[0028]

[Preferred Embodiments of the Invention] The preferred embodiments of the present invention will be described below.

[0029] In the method for forming a metal wiring in accordance with the present invention, the CMP process consisting of the first polishing step and second polishing step is implemented by the two following methods. The first polishing method will be initially described.

[0030] The first polishing method comprises a first polishing step in which polishing is conducted so that the metal film for wiring partially remains on the surface outside the recess and a second polishing step in which polishing is conducted till the surface of the electrically

insulating film outside the recess is almost entirely exposed, by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no less than 1 and no more than 3.

[0031] As mentioned above, when the difference in the density of wiring patterns is large, polishing typically proceeds faster in the regions with a high wiring density than in the regions with a low wiring density (low-density wiring regions) such as the regions which are close to the regions with isolated wiring or wiring-free regions. For this reason, the electrically insulating film present between wirings in the region with a high wiring density is polished excessively together with the metal located in the recess, as compared with the regions with a low-density wiring. Such a difference in polishing between the regions results in erosion. Accordingly, in the first polishing process, as shown in FIG. 3(a), if CMP is conducted so that the metal film 25 for wiring partially remains on the surface outside the recess formed in the electrically insulating film 24, then the metal film 25 for wiring will partially remain in the low-density wiring regions and polishing can be stopped before the electrically insulating film 23 present between the wirings of regions with a high wiring density will be polished.

[0032] In the first polishing step, the metal film 25 for wiring preferably remains at a surface area ratio of no less than 5% and no more than 30%, more preferably, no more than 10% of the substrate surface containing no recess. In the first polishing step, the surface area of metal film 25 for wiring which is present on the substrate can be measured in the manner as follows.

[0033] The instant when the region with the lowest pattern density is exposed within a region with the lowest polishing rate on the polishing surface is considered as the initial point of polishing operation. The polishing surfaces are observed in advance in an optical microscope in several polishing time points within the interval from the initial point of polishing to the instant the barrier metal is first exposed. The correlation between the polishing time and the surface area of the remaining metal film for wiring is then found by image processing. Then, in the actual polishing for wiring formation, the metal film for wiring with the surface area almost equal to the prescribed surface area can be left by conducting polishing only within the time period corresponding to the prescribed surface area of the remaining metal film for wiring from the instant the barrier metal film was exposed. The instant the barrier metal film is first exposed can be easily evaluated by detecting the rotation torque. Further, the above-mentioned initial point of polishing operation is equivalent to the instant the entire electrically insulating film outside the recess is exposed.

[0034] In the second polishing step, which is implemented after the first polishing step has been conducted in the above-described manner, polishing is conducted till the surface of the electrically insulating film outside the recess is almost entirely exposed, by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no less than 1 and no more than 3. If the polishing rate ratio (wiring metal to the barrier metal) of the polishing slurry is less than 1, that is, if the polishing rate of metal film for wiring is less than the polishing rate of barrier metal film, then it is difficult to remove the entire metal film for wiring, which partially remains on the surface and the wirings are short circuited by polishing residues. In order to prevent short circuiting, the polishing time has to be increased which results in a decreased throughput. Moreover, extending the polishing time creates a problem of overpolishing (eroding)

the region where the barrier metal or electrically insulating film has been exposed by primary polishing. On the other hand, if the polishing rate ratio (wiring metal to barrier metal) of polishing slurry exceeds 3, that is, if the polishing rate of metal film for wiring is much higher than the polishing rate of barrier metal film, then the wiring metal present in the recess is polished excessively causing the above-mentioned ditching. Moreover the barrier metal easily remains on the electrically insulating film because of a low polishing rate of the barrier metal, thereby causing short circuiting between the wirings. In order to prevent short circuiting, the polishing time has to be increased which results in a decreased throughput and further enhances ditching. Therefore, if the CMP is conducted in the second polishing step by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no less than 1 and no more than 3, the embedded wiring can be formed at a high throughput and without leaving a metal on the electrically insulating film outside the recess. Moreover, ditching can be prevented and erosion can be controlled through the first and second polishing steps. It is even more preferred that the polishing rate ratio (wiring metal to barrier metal) of the polishing slurry used in the second polishing step be no less than 1.5 and no more than 2.5.

[0035] The second polishing method of CMP in the method for forming a metal wiring in accordance with the present invention will be described below.

[0036] The second polishing method comprises a first polishing step in which polishing is conducted by using a polishing slurry comprising a polishing material, an oxidizing agent, an organic acid, and an alkanolamine represented by the above-described general formula (1), so that the metal film for wiring does not remain on the surface outside the recess and so that the barrier metal film is not completely removed by polishing, and a second polishing step in which polishing is conducted till the surface of the electrically insulating film outside the recess is almost entirely exposed, by using a polishing slurry such that the polishing rate ratio of the wiring metal to the barrier metal is no more than 1.

[0037] In the first polishing step of the second polishing method, CMP is conducted so that the metal film for wiring does not remain on the surface outside the recess and so that the barrier metal film is not completely removed by polishing. For this reason, polishing has to be conducted by using a polishing slurry comprising a polishing material, an oxidizing agent, an organic acid, and an alkanolamine represented by the above-described general formula (1) (referred to as an alkanolamine-containing slurry hereinbelow). Using such an alkanolamine-containing slurry can produce a film substantially stopping polishing of the metal film for wiring, as shown in FIG. 3(b) and can prevent erosion. In the first polishing step, in order to suppress excess polishing (ditching) of wiring metal inside the recess, the polishing is preferably stopped so that the barrier metal film remains on the electrically insulating film outside the recess, that is, before the electrically insulating film is exposed.

[0038] In the subsequent second polishing step, the CMP is conducted by replacing the above-mentioned alkanolamine-containing slurry with a polishing slurry which has a polishing rate ratio of wiring metal to barrier metal of no higher than 1, that is, which has a polishing rate of barrier metal film higher than that of wiring metal film. As a result, an embedded wiring can be obtained in which not only ditching is prevented, but also erosion is suppressed. As mentioned above, erosion occurs when the polishing rate of the wiring metal embedded in the recess is

higher than that of barrier metal film or electrically insulating film. In the second polishing step of the second polishing method, the polishing rate of metal film for wiring is less than that of barrier metal film which has remained in the first polishing step. Therefore, erosion is prevented.

[0039] In order to prevent excess cutting of barrier metal film and to polish uniformly the metal film for wiring, it is preferred that the polishing rate ratio (wiring metal to barrier metal) of the metal film for wiring to the barrier metal film of the polishing slurry used in the first polishing step be controlled so as to be no less than 30, preferably, no less than 50, even more preferably, no less than 100.

[0040] The alkanolamine-containing slurry used in the second polishing method, as described above, enhances the function of the barrier metal film as a polishing stopper in polishing the metal film for wiring and effectively prevents the occurrence of erosion. Therefore, it can be also used as the preferred polishing slurry in the first polishing step of the above-described first polishing method.

[0041] Further, in the first and second polishing methods, from the standpoint of polishing efficiency, it is preferred that the polishing rate (of metal film for wiring) of the polishing slurry used in the first polishing step be controlled so as to be no less than 300 nm/min, even more preferably, no less than 400 nm/min. From the standpoint of polishing accuracy and ditching prevention, it is preferred that this rate be controlled so as to be no higher than 1000 nm/min.

[0042] Examples of alkanolamines represented by the general formula (1) include methanolamine, dimethanolamine, trimethanolamine, ethanolamine, diethanolamine, triethanolamine, propanolamine, dipropanolamine, tripropanolamine, butanolamine, dibutanolamine, tributanolamine, N-methylethanolamine, N-ethylethanolamine, N-propylethanolamine, and N-butylethanolamine. The preferred among those alkanolamines are ethanolamine, diethanolamine, and triethanolamine, and triethanolamine is even more preferred because of its high solubility in aqueous media and high efficiency in decreasing the polishing rate of barrier metal film.

[0043] In terms of suppressing the polishing of barrier metal film, it is preferred that the content of the above-mentioned specific alkanolamine be no less than 0.01 wt.%, more preferably, no less than 0.2 wt.%, and even more preferably, no less than 0.5 wt.%, based on the entire slurry for polishing. Further, from the standpoint of suppressing the excess increase in the pH of slurry for polishing, it is preferred that the content of alkanolamine be no more than 10 wt.%, preferably no more than 5 wt.%, even more preferably, no more than 2 wt.%.

[0044] The alkanolamine contained in the polishing slurry apparently penetrated between the polishing abrasive grains and the polishing surface of the barrier metal film, thereby improving lubrication of the polishing surface. Therefore, if an alkanolamine-containing slurry is used, sliding of polishing abrasive grains over the polishing surface is improved and the mechanical polishing effect of the polishing abrasive grains is apparently decreased. In case of a barrier metal film consisting of a chemically stable metal such as a tantalum-type metal or the like, CMP of the tantalum-containing metal film is mainly governed by mechanical polishing and the contribution of chemical polishing is relatively small. Therefore, using the alkanolamine-

containing slurry makes it possible to suppress mechanical polishing of barrier metal film, that is, decreases the polishing rate of barrier metal film. On the other hand, in CMP of metal film for wiring, the contribution of chemical polishing conducted by the oxidizing agent is large and the polishing rate of metal film for wiring does not decrease too much. As a result, using the alkanolamine-containing slurry makes it possible to reduce the polishing rate of barrier metal film and, at the same time, to increase the difference in the polishing rate between the barrier metal film and metal film for wiring. Therefore, in the polishing of metal film for wiring, the function of the barrier metal film as a stopper film (polishing stopper) is enhanced.

[0045] The polishing slurry which is to be preferably used in the second polishing step of the first and second polishing methods will be described below.

[0046] In the methods for the formation of metal wiring in accordance with the present invention, a polishing slurry whose polishing rate ratio (wiring metal to barrier metal) can be controlled to less than 1 and no more than 3 in the first polishing method and to no more than 1 in the second polishing method is used as a polishing slurry employed in the second polishing step. Furthermore, it is preferred that a polishing slurry whose polishing rate ratio of the electrically insulating film to the barrier metal can be controlled to no less than 0.01 and no more than 0.5 be employed in both the first polishing method and in the second polishing method as the polishing slurry employed in the second polishing step.

[0047] Within the framework of the conventional technology, the only possible way to obtain a polishing rate ratio (wiring metal to barrier metal) of no more than 3 or no more than 1 when a chemically stable metal (for example, a metal with a high resistance to oxidation), such as tantalum-type metal, was used for the barrier metal film, was to decrease the quantity of oxidizing agent or to add an oxidation-preventing agent, thereby reducing the polishing rate of wiring metal. With such a method, the polishing rate of barrier metal film remains low and polishing residues easily appear, causing short circuiting between the wirings. If the polishing time is extended to prevent short circuiting, throughput is decreased. On the other hand, if the mechanical polishing action is intensified too much, the polishing surface is scratched or eroded. Accordingly, in the polishing steps of the method for forming a metal wiring in accordance with the present invention, a polishing slurry is employed whose polishing rate ratio (wiring metal to barrier metal) can be controlled to the desired level by increasing the polishing rate of barrier metal film.

[0048] There are two types of such polishing slurries. The first slurry will be initially described.

[0049] The first slurry comprises a silica polishing material, a carboxylic acid represented by the above-described formulas (2) or (3) (referred to as a polycarboxylic acid hereinbelow), and water. Furthermore, it is preferred that the first slurry also contains an oxidizing agent in order to enhance polishing of the metal film for wiring that was formed on the barrier metal film.

[0050] Abrasive particles consisting of silicon dioxide such as fumed silica, colloidal silica, and the like can be used as the silica polishing material. The silica polishing material can be prepared by a variety of conventional methods. For example, fumed silica can be obtained by vapor-phase synthesis of silicon tetrachloride in an oxygen – hydrogen flame, and silica can be manufactured

by hydrolysis of metal alkoxides in a liquid phase. In the manufacture of semiconductor devices, among abrasive grains consisting of silica dioxide of those types, fumed silica is preferably used because of its low cost and a small content of Na, which is an impurity.

[0051] The average particle size of silica polishing material is preferably no less than 5 nm, more preferably, no less than 50 nm, and preferably no more than 500 nm, more preferably, no more than 300 nm, as measured by a light scattering diffraction method. As for the particle size distribution, the maximum particle diameter (d100) is preferably no more than 3 μm , more preferably, no more than 1 μm . Furthermore, the specific surface area, as measured by the B.E.T. method, is preferably no less than 5 m^2/g , more preferably, no less than 20 m^2/g , and preferably no more than 1000 m^2/g , more preferably, no more than 500 m^2/g .

[0052] The content of the silica polishing material in the polishing slurry is appropriately set within a range of 0.1-50 wt.% based on the total weight of slurry composition. This range is determined by taking account of polishing efficiency and polishing accuracy. Preferably, the content of silica polishing material is no less than 1 wt.%, still more preferably, no less than 2 wt.%, and even more preferably, no less than 3 wt.%. As for the upper limit, this content is preferably no more than 30 wt.%, more preferably, no more than 10 wt.%, still more preferably, no more than 8 wt.%.

[0053] The polycarboxylic acid employed in the first slurry is a carboxylic acid containing no less than two carboxylic groups in a molecule. Examples of such acids include oxalic acid, malonic acid, tartaric acid, malic acid, glutaric acid, citric acid, and maleic acid, salts thereof, and mixtures of two or more thereof.

[0054] From the standpoint of increasing the polishing rate of tantalum-type metals, the content of the polycarboxylic acid is preferably no less than 0.01 wt.%, more preferably, no less than 0.05 wt.% based on the entire weight of slurry composition. From the standpoint of suppressing thixotropic properties of polishing slurry, it is preferred that the content of polycarboxylic acid be no more than 1 wt.%, yet more preferably, no more than 0.8 wt.%.

[0055] Because the first slurry contains silica abrasive grains as a polishing material and also contains the above-mentioned polycarboxylic acid, the polishing rate of tantalum-type metal films can be greatly increased, while protecting the polishing surface from damages. As a result, increasing the polishing rate of tantalum-type metal film can reduce the difference in polishing rate between the barrier metal film and metal film for wiring. Therefore, the occurrence of ditching and erosion can be prevented without decreasing the throughput, and high-quality embedded wiring can be formed.

[0056] The above-mentioned polycarboxylic acids demonstrate a cohesive (flocculation) action with respect to silica particles dispersed in water and the silica particles that were caused to cohere by the carboxylic acid enhance the mechanical effect, thereby apparently allowing for good polishing of barrier metal film. Further, because the cohesive effect is appropriately weak and comparatively soft particle aggregates are formed, the polishing rate of barrier metal film supposedly can be increased, while protecting the polishing surface from damages.

[0057] The second slurry will be described below.

[0058] The second slurry contains a silica polishing material, an inorganic salt, and water.

[0059] Examples of inorganic salts include at least one salt selected from the group including hydrogenacid salts, oxo acid salts, peroxy acid salts, and halogen oxo acid salts.

[0060] Example of hydrogen acid salts include salts of hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, hydrogen sulfide, hydrocyanic acid, hydrazoic acid, aurochloric acid, platinochloric acid, and the like.

[0061] Examples of oxo acid salts include salts of sulfuric acid, nitric acid, phosphoric acid, carbonic acid, boric acid, uranic acid, chromic acid, tungstic acid, titanilic acid, molybdenic acid, and the like.

[0062] Examples of peroxy acid salts include salts of peroxy monosulfuric acid, peroxy disulfuric acid, peroxy nitric acid, peroxy monophosphoric acid, peroxy diphosphoric acid, peroxy monocarbonic acid, peroxy dicarbonic acid, peroxy boric acid, peroxy uranic acid, peroxy chromic acid, peroxy tungstic acid, peroxy titanilic acid, peroxy molybdenic acid, and the like.

[0063] Examples of halogen oxo acid salts include salts of perchloric acid, perbromic acid, periodic acid, and the like.

[0064] The peroxy acid and halogen oxo acid salts are preferred because they act as oxidizing agents and chemically increase the polishing rate of metal film for wiring. Thus, they can be used as substituents for or auxiliaries to oxidizing agents added to the polishing slurries used in the fabrication of semiconductor devices

[0065] At least one salt selected from the group including salts containing ammonium ion, salts containing alkali metal ions, salts containing alkaline earth metal ions, salts containing group IIIB metal ions, salts containing group IVB metal ions, salts containing groups VB metal ions, and salts containing transition metal ions can be used as the inorganic salt.

[0066] Examples of alkali metal ions include Li ion, Na ion, K ion, Rb ion, Cs ion, Fe ion, and the like. Examples of alkaline earth metal ions include Be ion, Mg ion, Ca ion, Sr ion, Ba ion, Ra ion, and the like. Examples of group IIIB metal ions include Al ion, Ga ion, In ion, Tl ion, and the like. Examples of IVB metal ions include Sn ion, Pb ion, and the like. Examples of VB metal ions include Bi ion, and the like. Examples of transition metal ions include Sc ion, Ti ion, V ion, Cr ion, Mn ion, Fe ion, Co ion, Ni ion, Cu ion, Zn ion, Y ion, Zr ion, Nb ion, Mo ion, Tc ion, Ru ion, Rh ion, Pd ion, Ag ion, Cd ion, ions of lanthanides such as La, and the like, Hf ion, Ta ion, W ion, Re ion, Os ion, Ir ion, Hg ion, and ions of actinides such as Ac and the like.

[0067] Among the above-mentioned inorganic salts, potassium salts and ammonium salts are preferred. Examples of especially preferred salts include potassium sulfate, ammonium sulfate,

potassium chloride, potassium peroxo disulfate, ammonium peroxo disulfate, and ammonium periodate.

[0068] Further, two or more of the above-mentioned inorganic salts may be used together. Further, when semiconductor devices are fabricated, it is preferred that no inorganic salts of Na and heavy metals be present. This is because Na easily reacts with Si and easily adheres to and remains on Si substrates even after cleaning. Heavy metals also easily remain on Si substrates.

[0069] From the standpoint of increasing the polishing rate of barrier metal film, it is preferred that the content of the inorganic salt be no less than 0.01 wt.%, even more preferably, no less than 0.05 wt.% based on the total weight of slurry composition. As for the upper limit, in order to suppress the development of thixotropic properties in the polishing slurry, it is preferred that the content of the inorganic salt be no more than 10 wt.%, preferably, no more than 5 wt.%. When inorganic salts of two or more types are used, the aforesaid content means a total content of the salts.

[0070] The silica polishing material can use the polishing grains similar to those of the first slurry in the amount similar to that used in the first slurry.

[0071] Because the second slurry contains silica abrasive grains and an inorganic salt, the polishing rate of barrier metal film can be greatly increased, while protecting the polishing surface from damages. As a result, increasing the polishing rate of barrier metal film makes it possible to reduce the difference in polishing rate between the barrier metal film and metal film for wiring. Therefore, the occurrence of ditching and erosion can be prevented without decreasing the throughput, and high-quality embedded wiring can be formed.

[0072] The above-mentioned inorganic acid salts demonstrate a cohesive (flocculation) action with respect to silica particles dispersed in water and the silica particles that were caused to cohere by the carboxylic acid enhance the mechanical effect, thereby apparently making possible good polishing of barrier metal film. Further, because the cohesive effect is appropriately weak and comparatively soft particle aggregates are formed, the polishing rate of barrier metal film supposedly can be increased, while protecting the polishing surface from damages.

[0073] With the CMP using the above-described first and second slurry, it is possible to form an embedded wiring with high reliability and excellent electric properties at a high polishing rate, that is, at a high throughput, without causing ditching or erosion. Further, a slurry containing any of the polycarboxylic acids and inorganic acid salts, which are the main components of the first and second slurries, may be used.

[0074] It is preferred that the first and second slurries be capable of controlling the polishing rate of barrier metal film to no less than 25 nm/min, more preferably, to no less than 30 nm/min, even more preferably, to no less than 35 nm/min. As for the upper limit, especially with the first polishing method, it is preferred that the slurries be capable of controlling the polishing rate of barrier metal film to no more than 100 nm (sic), more preferably, to no more than 80 nm (sic), still more preferably, to no more than 70 nm (sic).

[0075] Furthermore, the first and second slurries can be advantageously used in the above-described first and second polishing method in which the polishing process is conducted in two stages. However, even when the polishing process is implemented in one stage, adjusting the polishing rate ratio (wiring metal to barrier metal) makes it possible to form an embedded wiring with high reliability and excellent electric properties which are superior to those obtained with the conventional technology. Moreover, the throughput is also higher and the occurrence of ditching and erosion is prevented. The polishing rate ratio (wiring metal to barrier metal) preferable when polishing is conducted in one stage, is close to 1. More specifically, this ratio is preferably no less than 0.5, and more preferably, no less than 0.8. As for the upper limit, this ratio is preferably no more than 2, more preferably, no more than 1.5, and still more preferably, no more than 1.2.

[0076] The first slurry, the second slurry, and the above-described alkanolamine-containing slurry will be described below in greater detail.

[0077] In the first slurry and second slurry, polishing abrasive grains consisting of silica should be the main component of polishing material. However, in the alkanolamine-containing slurry, the polishing material is not limited to the silica-type material, and polishing materials of various types can be used. Examples of abrasive grains that can be used include alumina such as α -alumina, θ -alumina, γ -alumina, fumed alumina, and the like, silica such as fumed silica, colloidal silica, and the like, titania, zirconia, germania, ceria, and mixtures consisting of no less than two types of abrasive grains selected from those metal oxide abrasive grains. Among them, silica and alumina are preferred.

[0078] As for the pH of polishing slurry, from the standpoint of polishing rate, corrosion, slurry viscosity, and stability of polishing agent dispersion, it is preferred that the pH value be no less than 4, preferably, no less than 5, and also no more than 9, preferably, no more than 8.

[0079] The pH value of the polishing slurry can be adjusted by the conventional methods. For example, an alkali can be directly added to the slurry in which the polishing material is dispersed and an organic acid is dissolved. Alternatively, part of the alkali which is to be added, or the entire alkali may be added together with an alkali salt of an organic acid. Examples of suitable alkalis include alkali metal hydroxides such as sodium hydroxide, potassium hydroxide, and the like, alkali metal carbonates such as sodium carbonate, potassium carbonate, and the like, ammonia, amines, and the like.

[0080] An oxidizing agent is preferably added to the polishing slurry in order to enhance polishing of the metal film for wiring which is formed on the barrier metal film. However, in the second polishing method, when the metal film for wiring located on the barrier metal film outside of the recess has been completely removed in the first polishing step, the polishing slurry used in the second polishing step may contain no oxidizing agent.

[0081] The oxidizing agent can be appropriately selected from the conventional water-soluble oxidizing agents by taking account of the type of electrically conductive metal film, polishing accuracy, and polishing efficiency. For example, examples of oxidizing agents causing no heavy metal ion contamination include peroxides such as H_2O_2 , Na_2O_2 , Ba_2O_2 , $(\text{C}_6\text{H}_5\text{C})_2\text{O}_2$, and the

like, and organic peroxides such as hypochlorous acid (HClO), perchloric acid, nitric acid, ozone water, peracetic acid, nitrobenzene, and the like. Among them, hydrogen peroxide (H₂O₂) is especially preferred because it contains no metal components and produces no toxic byproducts. In order to obtain a sufficient effect, it is preferred that the quantity of oxidizing agent contained in the polishing slurry be no less than 0.01 wt.%, more preferably, no less than 0.05 wt.% based on the entire weight of the polishing slurry. From the standpoint of preventing the occurrence of ditching and adjusting the polishing rate to the appropriate level, it is preferred that the quantity of oxidizing agent be no more than 15 wt.%, preferably, no more than 10 wt.%. Further, when an oxidizing agent is used which undergoes significant changes with time, as hydrogen peroxide does, a solution containing an oxidizing agent at the prescribed concentration and a composition that will produce the prescribed polishing slurry upon addition of the solution containing the oxidizing agent are prepared separately and the two components are mixed together just before the usage.

[0082] In order to enhance oxidation induced by the oxidizing agent, and to provide for stable polishing, a well known organic acid such as a carboxylic acid, amino acid, and the like may be added as a proton-donating agent. The polycarboxylic acids represented by formulas (2) and (3) can function as the proton-donating agents, but other organic acids such as carboxylic acid, amino acids, and the like may be also used.

[0083] Examples of carboxylic acids, other than polycarboxylic acids represented by formulas (2) and (3), include formic acid, acetic acid, propionic acid, butyric acid, valeric acid, acrylic acid, lactic acid, succinic acid, nicotinic acid, and salts thereof.

[0084] Examples of amino acids include L-glutamic acid, D-glutamic acid, L-glutamic acid monohydrochloride, L-glutamic acid sodium monohydrate, L-glutamine, glutatine, glycyl glycine, DL-alanine, L-alanine, β -alanine, D-alanine, γ -alanine, γ -aminobutyric acid, ϵ -aminocaproic acid, L-arginine monohydrochloride, L-asparagic acid, L-asparagic acid monohydrate, L-asparagic acid potassium salt, L-asparagic acid potassium trihydrate, D-asparagic acid, L-citrulline, L-tryptophane, L-threonine, L-alginin, glycine, L-cystein, L-cystein hydrochloride monohydrate, L-oxypoline, L-isoleucin, L-leucin, L-lysin monohydrochloride, DL-methionine, L-methionine, L-orthinine (sic) hydrochloride, L-phenylalanine, D-phenylglycine, L-proline, L-serine, L-tyrosine, L-valine, and the like.

[0085] From the standpoint of obtaining a sufficient effect of the organic acid as a proton-donating agent, it is preferred that the content of the organic acid be no less than 0.01 wt.%, more preferably, no less than 0.05 wt.% based on the total weight of the polishing slurry. From the standpoint of suppressing the occurrence of ditching and adjusting the polishing rate to the prescribed level, it is preferred that the content of the organic acid, including the content of the polycarboxylic acid represented by formula (2) or (3), be no more than 5 wt.%, preferably, no more than 3 wt.%.

[0086] When the oxidizing agent is added to the polishing slurry, an oxidation-preventing agent may be also added. Adding the oxidation-preventing agent facilitates the adjustment of polishing rate of electrically conductive metal films and also prevents the occurrence of ditching by forming a coating on the surface of electrically conductive metal film.

[0087] Examples of oxidation-preventing agents include benzotriazole, 1,2,4-triazole, benzofloxane (sic), 2,1,3-benzothiazole, o-phenylenediamine, m-phenylenediamine, catechol, o-aminophenyl, 2-mercaptobenzothiazole, 2-mercaptobenzoimidazole, 2-mercaptobenzoxazole, melanin, and derivatives thereof. Among them, benzotriazole and derivatives thereof are preferred. Examples of benzotriazole derivatives include substituted benzotriazoles having a hydroxyl group, an alkoxy group such as methoxy or ethoxy, an amino group, a nitro group, an alkyl group such a methyl group and ethyl group, or a halogen substituents such as fluorine, chlorine, bromine, and iodine in the benzene ring. Other examples include naphthalene triazole, naphthalene bi-triazole, and substituted naphthalene triazole and naphthalene bi-triazole that have been substituted in the same manner as described above.

[0088] From the standpoint of producing a sufficient effect, the content of such oxidation-preventing agent is preferably no less than 0.0001 wt.%, more preferably, no less than 0.001 wt.% based on the entire weight of polishing slurry. From the standpoint of adjusting the polishing rate to the appropriate level, it is preferred that the content of the oxidation-preventing agent be no more than 5 wt.%, preferably, no more than 2.5 wt.%, based on the entire weight of polishing slurry.

[0089] Various additives such as dispersing agents, buffer agents, viscosity-adjusting agents, and the like, that have been widely used as additives to polishing slurries, may be also added to the polishing slurry employed in accordance with the present invention, within a range producing no degrading effect on the slurry properties.

[0090] Typical methods for the manufacture of polishing slurry compositions containing free abrasive particles can be employed for the manufacture of the above-described polishing slurry. Thus, particles of polishing material are mixed in an appropriate amount with a dispersion medium and, if necessary, a protective agent is admixed in an appropriate amount. In this state, the surface of polishing material particles actively adsorbs air and has poor wettability, which results in a cohered state. The particles are therefore dispersed to obtain a primary particle state of the cohered particles of polishing material. Usual dispersing methods and apparatuses can be used in the dispersing process. More specifically, dispersing can be conducted by the conventional method by using, for example, an ultrasonic dispersing apparatus, various bead mill dispersing machines, kneaders, ball mills, and the like. Further, inorganic salts and polycarboxylic acids represented by formulas (2) and (3) sometimes increase thixotropy at the same time as they increase flocculation of silica particles. Therefore, in order to conduct good dispersing, the acids and salts are preferably added and mixed after completion of dispersing.

[0091] Polishing by the CMP method in accordance with the present invention can be conducted, for example, by using the following typical CMP apparatus. Wafers with a metal film for wiring deposited thereon are arranged in a spindle-type wafer carrier. The wafer surface is brought in contact with a polishing pad composed of a porous urethane pasted on a rotating plate (board), and polishing is conducted by rotating the wafers and the polishing pad with respect to each other, while supplying the polishing slurry from the slurry supply orifice. If necessary, a pad conditioner can be brought in contact with the polishing pad surface to condition the polishing pad surface.

[0092] Final operation of polishing in the CMP process will be described below.

[0093] In the first polishing step of the first polishing method, as described above, polishing is completed after the prescribed time has elapsed from the moment the barrier metal film was first exposed, this time being estimated based on the relationship between the polishing time and the surface area of metal film for wiring that has been determined in advance.

[0094] Polishing in other polishing steps is completed, for example, in the manner as follows.

[0095] In the first example, the polishing rate of a metal film is measured in advance, the time required for removing the metal film of the prescribed thickness is computed, and polishing is ended after the prescribed time has elapsed from the instant the computed time has elapsed from the polishing starting time.

[0096] In the second example, the CMP is conducted, while measuring the polishing rate, and polishing is ended after the prescribed time has elapsed from the instant the polishing rate started to decrease rapidly.

[0097] In the third example, a rotation torque meter is set on the rotary shaft of a rotary plate and the CMP is conducted, while measuring changes of the rotation torque applied to the rotary shaft. The polishing is ended after the prescribed time has elapsed from the instant the changes of the rotation torque accompanying the removal of the metal film and exposure of the barrier metal film has been detected.

[0098] In the fourth example, the polishing surface is illuminated with light and the CMP is conducted, while measuring the intensity of reflected light. Thus, if the polishing proceeds from the metal film for wiring into the barrier metal film and electrically insulating film, then the material present on the polishing surface undergoes changes. Therefore, the intensity of reflected light also changes. The polishing is ended after the prescribed time has elapsed from the instant the reflected light intensity started to change.

[0099] Further, the end point of polishing may be also determined by appropriately combining the above-described methods.

[0100] In the above-described method for forming a metal wiring in accordance with the present invention, a silicon oxide film, a BPSG film, and a SOG film can be considered as an electrically insulating film, and copper, silver, gold, platinum titanium, tungsten, aluminum, and alloys thereof can be employed as wiring metals. Further, Ta, TaN, Ti, TiN, W, WN, WSiN, and the like can be employed as the barrier metal. The method for forming a metal wiring in accordance with the present invention is especially suitable for forming the metal wiring when the metal for wiring is copper or a copper-based alloy and the barrier metal film is a Ta film or TaN film.

[0101] The method for forming a metal wiring in accordance with the present invention is suitable for the formation of various conventional embedded wirings, for example, upper wiring layers in multilayer wiring structures, dual damascene wiring, and the like.

[0102]

[Embodiments] The present invention will be described below in greater detail based on embodiments thereof.

[0103] (Fabrication of substrate for CMP) First, a lower wiring layer consisting of a silicon oxide film having a lower wiring (not shown in the figures) was formed on a six-inch wafer (silicon substrate) having semiconductor elements, such as transistors, formed thereon. As shown in FIG. 1(a), a silicon nitride film 2 was then formed thereon, a silicon oxide film 3 with a thickness of about 500 nm was formed thereon, and wiring grooves and contact holes with a depth of 500 nm and a width of 0.23-10 μm were formed by patterning the silicon oxide film 3 by the usual photolithography process and reactive ion etching process. Then, as shown in FIG. 1(b), a Ta film (tantalum film) 4 with a thickness of 50 nm was formed by sputtering, then a copper film with a thickness of about 50 nm was formed by sputtering, and then a copper film with a thickness of about 800 nm was formed by plating.

[0104] First, in Embodiment 20, a Ta film was formed by sputtering on a six-inch silicon substrate for the purpose of measuring the polishing rate of Ta film (barrier metal film) and this substrate was used as the substrate for CMP.

[0105] (CMP conditions) CMP was conducted by using a SpeedFam-IPEC 372M machine. A polishing pad (Rodel-Knitter Co., IC1400) was bonded to a stationary plate of a polishing machine. Polishing was conducted under the following conditions: polishing load (contact pressure applied to the polishing pad) : 27.6 kPa, rotation speed of the board : 55 rpm, carrier rotation speed : 55 rpm, slurry-polishing liquid supply rate : 100 mL/min.

[0106] (Measurement of polishing rate) Four needle electrodes equidistantly arranged above the wafer were placed on a straight line, a constant current was passed between the two external probes, and the difference in potential generated between the two internal probes was measured. Then, electric resistance (R') was determined and multiplied by a correction factor RCF (resistivity correction factor) to find a surface resistivity (ρ_s') Then, surface resistivity was determined for which the thickness was known (T (nm)). Since surface resistivity is inversely proportional to thickness, the following relationship is valid: d (nm) = $(\rho_s \times T)/\rho_s'$, where d stands for a thickness corresponding to the surface resistivity ρ_s' . The thickness, d , could be calculated by this formula. Then, the polishing rate was calculated by dividing the difference in film thickness before and after polishing by the polishing time. A probe-type resistance meter (Loresta-GP) manufactured by Mitsubishi Kagaku K. K. was used for measuring the surface resistivity.

[0107] (Embodiments 1 – 6 : Second polishing method, alkanolamine-containing slurry) As shown in Table 1, polishing slurries (alkanolamine-containing slurries) were prepared that contained θ -alumina (manufactured by Sumitomo Chemical Industries Co., Ltd.; AKP-G008) 5 wt.%, citric acid (manufactured by Kanto Chemical Co., Ltd.) 1.5 wt.%, H_2O_2 (manufactured by Kanto Chemicals Co., Ltd.) 2.5 wt.%, triethanolamine (manufactured by Kanto Chemicals Co., Ltd.) 0.01-10 wt.% and having a pH of 5.5 that was adjusted with KOH. CMP was conducted by

using the polishing slurries till the entire copper film present on the electrically insulating film outside the recess was removed. Then, the polishing slurry was replaced with the below-described polishing slurry of Embodiment 21 (polishing rate ratio (Cu/Ta) = 0.15) and CMP was conducted till the entire surface of the electrically insulating film outside the recess was exposed.

[0108] In Comparative Example 1, polishing slurries were prepared in the same manner as in Embodiments 1 – 6, except that no triethanolamine was added, and CMP was conducted in one step.

[0109] The results obtained are presented in Table 1. Data presented in Table 1 clearly show that adding triethanolamine greatly decreased the polishing rate of Ta film. Further, SEM observation of the cross section of the substrate of the present embodiments confirmed that ditching and erosion have been suppressed.

[0110] (Embodiments 7, 8 : second polishing method, alkanolamine-containing slurries) As shown in Table 1, polishing slurries were prepared that were identical to that of Embodiment 3, except that diethanolamine or ethanolamine was used instead of triethanolamine, and CMP was conducted in a similar manner.

[0111] The results obtained are shown in Table 1. Data shown in Table 1 clearly show that adding diethanolamine or ethanolamine also greatly decreased the polishing rate of Ta film. Further, SEM observation of the cross section of the substrate of the present embodiments confirmed that ditching and erosion have been suppressed.

[0112] (Embodiment 9 : second polishing method, alkanolamine-containing slurries) As shown in Embodiment 9 of Table 1, a polishing slurry was prepared that was identical to that of Embodiment 3, except that fumed silica Qs-9 was used as the polishing abrasive grains instead of alumina, and CMP was conducted in a similar manner.

[0113] The results obtained are presented in Table 1. Data presented in Table 1 clearly show that adding triethanolamine also greatly decreased the polishing rate of Ta film when silica was used as the polishing abrasive grains. Further, SEM observations of the cross section of the substrate of the present embodiments confirmed that ditching and erosion have been suppressed.

[0114] (Embodiments 10 – 13 : second polishing method, alkanolamine-containing slurries) Polishing slurries were prepared that were identical to that of Embodiment 3, except that citric acid was replaced with organic acids shown in Embodiments 10 – 13 (sic), and CMP was conducted in a similar manner.

[0115] The results obtained are presented in Table 1. Data presented in Table 1 clearly show that adding triethanolamine also greatly decreased the polishing rate of Ta film when various organic acids other than citric acid were used. Further, SEM observation of the cross section of the substrate of the present embodiments confirmed that ditching and erosion have been suppressed.

[0116]

Table 1

	Polishing grains (wt.%)	Organic acid (wt.%)	Alkanolamine (wt.%)	Ta polishing rate (nm/min)
Embodiment 1	Alumina (5)	Citric acid (1.5)	Triethanolamine (0.01)	9.75
Embodiment 2	Alumina (5)	Citric acid (1.5)	Triethanolamine (0.50)	4.67
Embodiment 3	Alumina (5)	Citric acid (1.5)	Triethanolamine (1.00)	3.48
Embodiment 4	Alumina (5)	Citric acid (1.5)	Triethanolamine (2.00)	2.11
Embodiment 5	Alumina (5)	Citric acid (1.5)	Triethanolamine (5.00)	1.02
Embodiment 6	Alumina (5)	Citric acid (1.5)	Triethanolamine (0.01)	0.53
Embodiment 7	Alumina (5)	Citric acid (1.5)	Triethanolamine (10.00)	3.12
Embodiment 8	Alumina (5)	Citric acid (1.5)	Diethanolamine (1.00)	1.89
Embodiment 9	Silica (5)	Citric acid (1.5)	Ethanolamine (1.00)	2.11
Embodiment 10	Alumina (5)	Glutaric acid (1.5)	Triethanolamine (1.00)	3.69
Embodiment 11	Alumina (5)	Tartaric acid (1.5)	Triethanolamine (1.00)	3.45
Embodiment 12	Alumina (5)	Malic acid (1.5)	Triethanolamine (1.00)	3.53
Embodiment 13	Alumina (5)	Glycine (1.5)	Triethanolamine (1.00)	3.73
Comparative Example 1	Alumina (5)	Citric acid (1.5)	None	16.18

(Embodiments 14 - 19 : second polishing method, alkanolamine-containing slurries) Polishing slurries were prepared that were identical to those of Embodiments 1 - 6, except that a mixed acid containing 0.16 wt.% glutaric acid, 1.5 wt.% citric acid, and 0.3 wt.% glycine was used as the organic acid and benzotriazole was added at a ratio of 0.005 wt.% as the oxidation-preventing agent, and CMP was conducted in a similar manner.

[0117] In Comparative Example 2, polishing slurries were prepared that were identical to those of Embodiments 14 - 19, except that they contained no alkanolamine and CMP was conducted in one step.

[0018] The results obtained are presented in Table 2. Data presented in Table 2 clearly show that the polishing rate of Ta film was greatly increased and the ratio of the polishing rate of copper film to the polishing rate of Ta film was greatly increased. Thus, adding triethanolamine was found to increase polishing selectivity of copper film. Further, SEM observations of the cross section of the substrate of the present embodiments confirmed that ditching and erosion have been suppressed.

[0119]

[Table 2]

Table 2

	Polishing grains (wt.%)	Org. acid (wt.%)	Oxidn.-preventing agent (wt.%)	Alkanolamine (wt.%)	Ta polishing rate (nm/min)	Cu polishing rate (nm/min)	Cu polishing rate/ Ta polishing rate
Emb. 14	Alumina (5)	Mixed acid (1.96)	Benzotriazole (0.005)	Triethanolamine (0.01)	9.89	1040.5	105
Emb. 15	Alumina (5)	Mixed acid (1.96)	Benzotriazole (0.005)	Triethanolamine (0.50)	4.55	1013.2	223
Emb. 16	Alumina (5)	Mixed acid (1.96)	Benzotriazole (0.005)	Triethanolamine (1.00)	3.48	911.1	262
Emb. 17	Alumina (5)	Mixed acid (1.96)	Benzotriazole (0.005)	Triethanolamine (2.00)	2.05	808.8	395
Emb. 18	Alumina (5)	Mixed acid (1.96)	Benzotriazole (0.005)	Triethanolamine (5.00)	1.03	543.7	528
Emb. 19	Alumina (5)	Mixed acid (1.96)	Benzotriazole (0.005)	Triethanolamine (10.00)	0.47	387.6	825
Comp. Ex. 2	Alumina (5)	Mixed acid (1.96)	Benzotriazole (0.005)	None	15.32	1060.8	69

(Embodiment 20 : polishing of Ta film with the first slurry) In order to demonstrate the effect of polycarboxylic acids represented by formulas (2) and (3) in the polishing slurry, CMP of Ta films deposited by sputtering on six-inch silicon substrates was conducted by using various polishing slurries shown in Tables 3 – 5. The respective polishing rates were measured. Further, fumed silica Qs-9 manufactured by Takuyama Co., Ltd. was used as the silica polishing material. For comparison, slurry No. 1 contained no polycarboxylic acid. Table 3 shows the results obtained when glutaric acid was used as the polycarboxylic acid, and slurries of various types containing different amounts of this acid were employed. Table 4 shows the results obtained when glutaric acid was used as the polycarboxylic acid and polishing slurries of various types containing different pH-adjusting agents and having different pH values were employed. Table 5 shows the results obtained with polishing slurries containing various polycarboxylic acids.

[0120] Data presented in Table 3 demonstrate that adding glutaric acid greatly increased the polishing rate of Ta film and that increasing the amount of glutaric acid added to the slurry (content of glutaric acid in the slurry) resulted in the increased polishing rate.

[0121] Further, adding glutaric acid also changed the color of the polishing slurry from semitransparent to opaque. This result indicates that flocculation led to the formation of particles with a large diameter and scattering intensity was increased. The above-described results suggest that adding polycarboxylic acids results in the increased ion strength in the solution, pressure application to the electric double layer, and decrease in the electric repulsion forces acting

between the particles. Moreover, interaction of silica particles and polycarboxylic acid having no less than two carboxylic groups in a molecule causes cohesion (flocculation), and soft silica particles produced by the flocculation act as polishing material grains increasing the mechanical polishing effect and thereby raising the polishing rate of Ta film.

[0122] As shown in Table 3 and Table 4, polishing could be conducted at a high rate even when the pH value of polishing slurry was changed within a range of 4.5-6.5. Further, the results presented in Table 4 demonstrate that a similarly high polishing rate was attained even when KOH was replaced with NH_4OH as the pH-adjusting agent.

[0123] Data presented in Table 5 show that the polishing rate of Ta film could be increased when polycarboxylic acids with a specific structure represented by formulas (2) and (3) were used instead of glutaric acid. Further, adding any of carboxylic acids shown in the table also resulted in a transition from semitransparent to opaque polishing slurry.

[0124]

[Table 3]

Table 3

Slurry No.	Polishing material (content/wt.%)	Carboxylic acid (content/wt.%)	pH adjusting agent	pH	Ta polishing rate (nm/min)
1	Fumed silica (5 wt.%)	-	KOH	6.5	12.1
2	Fumed silica (5 wt.%)	Glutaric acid (0.02)	KOH	6.5	29.2
3	Fumed silica (5 wt.%)	Glutaric acid (0.04)	KOH	6.5	29.3
4	Fumed silica (5 wt.%)	Glutaric acid (0.08)	KOH	6.5	42.3
5	Fumed silica (5 wt.%)	Glutaric acid (0.16)	KOH	6.5	46.5
6	Fumed silica (5 wt.%)	Glutaric acid (0.27)	KOH	6.5	56.5

[0125]

[Table 4]

Table 4

Slurry No.	Polishing material (content/wt.%)	Carboxylic acid (content/wt.%)	pH adjusting agent	pH	Ta polishing rate (nm/min)
7	Fumed silica (5 wt.%)	Glutaric acid (0.16)	KOH	4.5	51.2
8	Fumed silica (5 wt.%)	Glutaric acid (0.16)	KOH	5.0	52.5
9	Fumed silica (5 wt.%)	Glutaric acid (0.16)	KOH	5.5	50
10	Fumed silica (5 wt.%)	Glutaric acid (0.16)	NH_4OH	4.5	50.9
11	Fumed silica (5 wt.%)	Glutaric acid (0.16)	NH_4OH	5.0	52.1
12	Fumed silica (5 wt.%)	Glutaric acid (0.16)	NH_4OH	5.5	49.3

[0126]

[Table 5]

Table 5

Slurry No.	Polishing material (content/wt.%)	Carboxylic acid (content/wt.%)	pH adjusting agent	pH	Ta polishing rate (nm/min)
13	Fumed silica (5 wt.%)	Malic acid (0.536)	KOH	5.5	58.8
14	Fumed silica (5 wt.%)	Tartaric acid (0.6)	KOH	5.5	36.1
15	Fumed silica (5 wt.%)	Maleic acid (0.46)	KOH	5.5	36.2
16	Fumed silica (5 wt.%)	Malonic acid (0.416)	KOH	5.5	46.9
17	Fumed silica (5 wt.%)	Oxalic acid (0.36)	KOH	5.5	48.2
18	Fumed silica (5 wt.%)	Citric acid (0.33)	KOH	6.5	97.1

(Embodiment 21 : one-step polishing with the first slurry) Various polishing slurries shown in Table 6 were prepared and the CMP was conducted in one step by using those polishing slurries till the entire surface of the electrically insulating film, outside the recess, was exposed. The polishing rate was measured for the copper film, Ta film, and silicon oxide film (SiO₂ insulating film).

[0127] The results obtained suggest that the polishing rate ratio of Ta film and copper film can be adjusted by changing the composition ratio of the polycarboxylic acid represented by formulas (2) and (3) or a mixture of such acids, the oxidizing agent (H₂O₂), and the oxidation-preventing agent (benzotriazole (BTA)). Within the framework of the conventional technology, the polishing rate ratio was adjusted by decreasing the polishing rate of copper film, whereas in accordance with the present invention the polishing rate can be adjusted (the difference in polishing rates can be decreased) also by increasing the polishing rate of Ta film. Therefore, throughput can be greatly increased.

[0128] Further, SEM observations of the substrate cross section confirmed that ditching and erosion could be suppressed. This result indicates that because the difference in the polishing rates between the copper film and Ta film was appropriately small, the excess polishing of copper film was prevented and that because of a sufficiently low polishing rate of the electrically insulating film, this film could act as a stopper, thereby preventing the occurrence of ditching and erosion. Further, SEM observations of polishing surface revealed no damages that could cause problems.

[0129]

[Table 6]

Table 6

Slurry No.	Polishing material (content/wt.%)	Carboxylic acid (content/wt.%)	Oxidn.-preventing agent (content/wt.%)	Oxidizing agent (content/wt.%)	pH adjusting agent	pH	Ta polishing rate (nm/min)	Cu polishing rate (nm/min)	SiO ₂ polishing rate (nm/min)
19	Fumed silica (8 wt.%)	Glutaric acid (0.16)	BTA (0.005)	H2O2 (0.093)	KOH	4.5	45.3	30.3	2.0
20	Fumed silica (8 wt.%)	GLU (0.16) + QUE * (0.05)	BTA (0.005)	H2O2 (1.53)	KOH	6.0	37	80.2	2.0
21	Fumed silica (8 wt.%)	Citric acid (0.05)	BTA (0.005)	H2O2 (1.53)	KOH	6.0	47	55.6	2.0

* GLU : glutaric acid, QUE : citric acid

(Embodiments 22 – 29 : one-step polishing with the second slurry) Polishing slurries having a pH value of 4.5 and containing 5 wt.% fumed silica Qs-9 manufactured by Tokuyama Co., Ltd., 0.1-3 wt.% potassium sulfate manufactured by Kanto Chemicals Co., Ltd. were prepared. The CMP was conducted in one step by using those polishing slurries till the entire surface of the electrically insulating film, outside the recess, was exposed. The polishing rate was measured for the copper film and Ta film.

[0130] Data presented in Table 7 clearly show that adding potassium sulfate made it possible to increase significantly the polishing rate of Ta film, without decreasing the polishing rate of copper film, and that increasing the amount (content) of potassium sulfate allowed the polishing rate of tantalum to be increased.

[0131] Further, the color of the polishing slurry was changed from semitransparent to opaque as a result of potassium sulfate addition. This result indicates that large-diameter particles were formed by cohesion and that the scattering intensity was increased. The above-described data suggest that adding inorganic salts results in the increased ion strength in the solution, pressure application to the electric double layer, and decrease in the electric repulsion forces acting between the fumed silica particles. Moreover, interaction between the inorganic salts causes cohesion (flocculation), and soft silica particles produced by the flocculation act as polishing material grains increasing the mechanical polishing effect and thereby raising the polishing rate of Ta film.

[0132]

[Table 7]

Table 7

	Potassium sulfate (wt.%)	Ta polishing rate (nm/min)	Cu polishing rate (nm/min)
Comparative example	0	25.7	8.1
Embodiment 22	0.10	32.1	not measured
Embodiment 23	0.25	39.9	not measured
Embodiment 24	0.50	50.3	not measured
Embodiment 25	0.75	58.5	not measured
Embodiment 26	1.00	67.2	9.8
Embodiment 27	2.00	97.1	not measured
Embodiment 28	2.50	105.1	not measured
Embodiment 29	3.00	109.2	11.8

(Embodiments 30, 31 : one-step polishing with the second slurry) Polishing slurries were prepared in the same manner as in Embodiment 26 and Embodiment 29, except that ammonium sulfate (Embodiment 30) and potassium chloride (Embodiment 31) were used instead of potassium sulfate. The CMP was conducted in the same manner and the polishing rate was measured. The results obtained are shown in FIG. 8.

[0133] Data presented in Table 8 demonstrated that the polishing rate of Ta film was also increased when ammonium sulfate and potassium chloride were added as inorganic salts other than potassium sulfate.

[0134]

[Table 8]

Table 8

	Inorganic salt	Concentration of inorganic salt (wt.%)	Ta polishing rate (nm/min)	Cu polishing rate (nm/min)
Embodiment 30	Ammonium sulfate	1.0	59.1	9.6
Embodiment 31	Potassium chloride	3.0	102.1	11.1

(Embodiments 32 – 37 : one-step polishing with the second slurry) Polishing slurries were prepared in the same manner as in Embodiments, 24, 26, or 27, except that various inorganic acids demonstrating the oxidation effect, which are shown in Table 9, were used instead of potassium sulfate, and the CMP was conducted by using those slurries. For comparison, in Embodiment 37, a polishing slurry was prepared which contained 2.5 wt.% hydrogen peroxide and potassium sulfate that is an inorganic salt demonstrating no oxidation effect. The results obtained in Embodiment 37 are presented in the table together with those obtained in Embodiment 36.

[0135] Data presented in Table 9 show that the polishing rate of tantalum was also increased when inorganic salts demonstrating oxidizing effect were added. Further, the oxidizing effect of those inorganic salts greatly increase the polishing rate of copper by comparison with that attained in Embodiment 26. Comparison with Embodiment 37 suggests that adding inorganic salts demonstrating an oxidizing effect increases the polishing rate of copper to the same degree as in the case when hydrogen peroxide was present in the slurry.

[0136]

[Table 9]

	Inorganic salt	Conc. of inorg. salt (wt.%)	Hydrogen peroxide (wt.%)	Ta polishing rate (nm/min)	Cu polishing rate (nm/min)
Emb. 32	Peroxo disulfuric acid, potassium salt	0.5	0	50.5	247.8
Emb. 33	Peroxo disulfuric acid, potassium salt	1.0	0	71.2	468.6
Emb. 34	Peroxo disulfuric acid, potassium salt	2.0	0	79.8	623.2
Emb. 35	Peroxo disulfuric acid, ammonium salt	1.0	0	68.3	480.3
Emb. 36	Ammonium periodate	1.0	0	69.5	470.0
Emb. 37	Potassium sulfate	1.0	2.5	70.8	472.2
Emb. 26	Potassium sulfate	1.0	0	67.2	9.8

(Embodiments 38 – 41 : one-step polishing with the second slurry) As shown in Table 10, polishing slurries were prepared which contained potassium sulfate, hydrogen peroxide manufactured by Kanto Chemicals Co., Ltd., oxalic acid or malic acid manufactured by Kanto Chemicals Co., Ltd., and benzotriazole manufactured by Kanto Chemicals Co., Ltd., and the CMP was conducted in one step by using those slurries. The results obtained in measuring the polishing rate are shown in Table 10.

[0137] Data shown in Table 10 suggest that changing the concentration of organic acid or oxidizing agent makes it possible to change the polishing rate of copper, while maintaining the polishing rate of tantalum, that is, to control the copper/tantalum polishing rate ratio, while maintaining the polishing rate of tantalum.

[0138] Further, SEM observations conducted on the substrate cross section demonstrated that ditching and erosion were suppressed. SEM observations conducted on the polishing surface revealed no damages that could cause problems.

[0139]

[Table 10]

Table 10

	Potassium sulfate (wt.%)	Hydrogen peroxide (wt.%)	Organic acid	Conc. of org. acid (wt.%)	Benzo-triazole (wt.%)	Ta polishing rate (nm/min)	Cu polishing rate (nm/min)
Emb. 38	1.0	2.5	Oxalic acid	0.1	0.001	65.2	29.8
Emb. 39	1.0	2.5	Malic acid	0.02	0.005	64.0	38.1
Emb. 40	1.0	2.5	Malic acid	0.03	0.005	64.3	65.2
Emb. 41	1.0	2.5	malic acid	0.04	0.005	64.7	100.5

(Embodiments 42 and 43 : one step polishing with the second slurry) Polishing slurries with compositions presented in Table 11 were prepared and one-step CMP was conducted by using those polishing slurries. The results obtained in measuring the polishing rate are presented in Table 11.

[0140] The results presented in the table demonstrate that replacing part of peroxy disulfuric acid potassium with potassium sulfate decreases the polishing rate of copper, while maintaining the polishing rate of Ta film. Therefore, it is clear that the polishing rate ratio of copper and Ta film can be adjusted by combining inorganic salts even without using the oxidizing agent.

[0141]

[Table 11]

	Potassium sulfate (wt.%)	Peroxo disulfuric acid potassium salt (wt.%)	Hydrogen peroxide (wt.%)	Organic acid	Conc. of org. acid (wt.%)	Benzo-triazole (wt.%)	Ta polishing rate (nm/min)	Cu polishing rate (nm/min)
Emb. 42	0	0.5	0	Malic acid	0.15	0.005	47.5	128.3
Emb. 43	0.25	0.25	0	Malic acid	0.15	0.005	48.1	71.2

(Embodiment 44 : first polishing method) In the first polishing step, CMP was conducted by using a polishing slurry of Embodiment 18, which contained triethanolamine. The polishing was stopped when the copper film with a surface area of about 15% of the substrate surface area, outside the recess, was left on the insulating film, outside the recess.

[0142] Then, in the second polishing step, CMP was conducted by using a polishing slurry No. 20, which was used in Embodiment 21, till the entire surface of the electrically insulating film, outside the recess, was exposed. It follows from Table 6 that the polishing rate ratio (Cu/Ta/silicon oxide) of the polishing slurry was 2.2/1/0.05.

[0143] When the substrate cross section was observed in SEM after polishing, it was found that ditching and erosion were almost completely prevented. Furthermore, SEM observations of the polishing surface revealed no damages that could cause problems.

[0144]

[Effect of the Invention] As described above, in accordance with the present invention, ditching and erosion are suppressed and a highly reliable embedded wiring with a small spread of wiring resistance can be formed.

[Brief Description of the Drawings]

FIG. 1 is a cross-sectional view illustrating the conventional method for forming a metal wiring.

FIG. 2 illustrates the cross-sectional shape of a wiring portion obtained when an embedded copper wiring was formed by the conventional method for forming a metal wiring.

FIG. 3 is a cross-sectional view of an embedded wiring layer, this figure illustrating the method for forming a metal wiring in accordance with the present invention.

[Legends]

1 – lower wiring layer; 2 – silicon oxide film; 3 – silicon oxide film; 4 – barrier metal film; 5 – copper film; 23 – electrically insulating film; 24 – barrier metal film; 25 – metal film for wiring

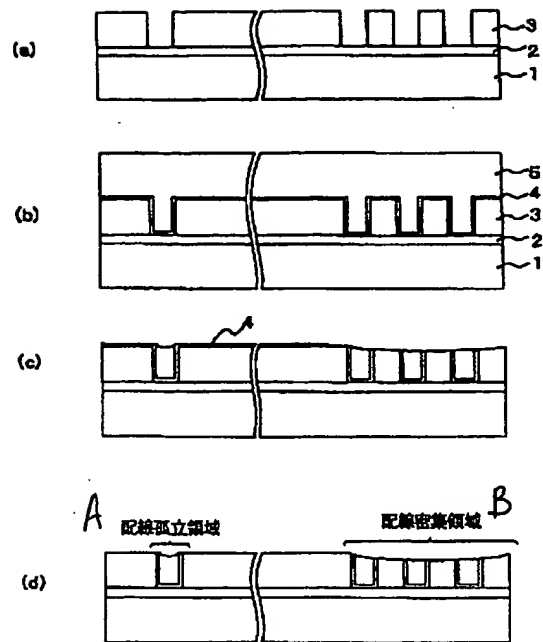


FIG. 1

A – region with isolated wiring; B – region with a high wiring density

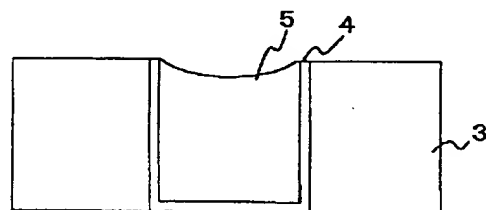


FIG. 2

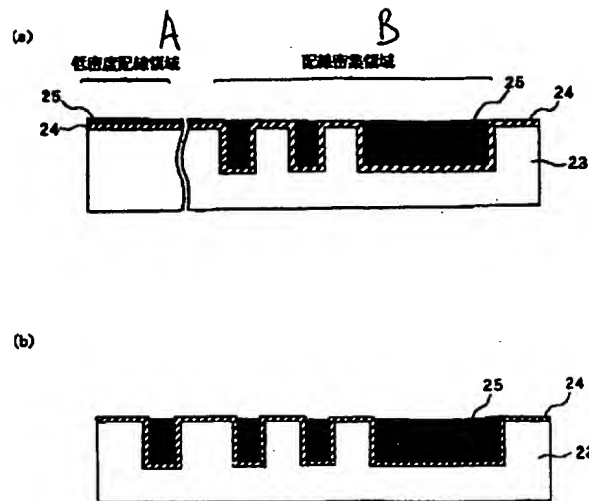


FIG. 3

A – region with a low wiring density; B – region with a high wiring density

Continued from the front pate

F theme (reference) 3C058 AA97 AC01 AC04 BC02 CA01
 CB01 CB03 DA12
 5F033 HH11 HH12 HH21 JJ11 JJ12
 JJ21 MM01 MM12 MM13 NN06
 NN07 PP15 PP26 PP33 QQ09
 QQ13 QQ37 QQ48 QQ49 QQ50
 RR04 WW00 XX00 XX01